$n - GaAs$ QUALITY DIAGNOSE FROM SHALLOW IMPURITIES PHOTOELECTRIC SPECTROSCOPY LINE SHAPES DEPENDENCE ON ELECTRIC FIELD

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Abstract

It is established experimentally that the low temperature photo-electric spectra line width of shallow impurities depends not only on charged impurity concentration $N_i = 2KN_A$ and degree of samples compensation $K = N_A/N_D$, as it was believed earlier.To a great extent it depends on the impurity distribution inhomogeneity also.For samples with homogeneous and inhomogeneous distribution of impurities line width dependence character on external electric fields, smaller than break down one, are different.This broadening mechanism allows to control the quality of samples with nearly equal impurity concentrations.

1   INTRODUCTION

Shallow impurities photoelectric spectroscopy (SIPS) of hydrogen like impurities consists in arising of lines in photoconductivity spectra of semicon-

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ductor, when electrons localized on impurities are photo excited resonantly. It is an effective method for investigations of SI in semiconductors[1]. Considerable information can be obtained from the investigations of the line broadening mechanisms [2-4] and experimental line width. Convenient for this purpose are optically allowed transition lines from the ground state of SI ($1s$) to excited Zeeman states $2p_{-1}$ and $2p_{+1}$ formed in magnetic field H. Even for available purest samples of Si, Ge, GaAs, InP the low temperature SI photoexcitation lines dominant broadening mechanism is concentration mechanism (inhomogeneous broadening). This broadening is the result of optical transition (for example $1s \rightarrow 2p_{+1}$) energy differences for all impurity atoms from that of isolated impurity atom owing to interaction with surrounding impurities. In particular, in compensated semiconductors ($K \geq 01$) with charged impurities concentration $N_i = 2KN_D$ comparable with N_D at moderate magnetic fields ($\gamma = h\omega_c/2Ry^* \sim 1$, $h\omega_c$-cyclotron energy, Ry^*-effective Ridberg), when quadrupole-electric field gradient broadening for $1s \rightarrow 2p_{\pm 1}$ lines is negligible[2], the broadening of $1s \rightarrow 2p_{+1}$ line arise from the quadratic Stark effect shift of levels by charged impurities electric fields E. Then the line shape would be determined by distribution of E^2 at the neutral donor center, which depends on charged impurity distribution in semiconductor.

Character of distribution of charged impurity around the optically active neutral donor depends on two factors. The first is the distribution of impurity atoms in semiconductor, which mainly is determined with growing technology (we consider the residual impurities only). The inhomogeneous in impurity distribution creates the random potential which is the potential of fluctuations. The influence of this potential on cyclotron resonance line shape was established [5] and was used for quality control of semiconductor samples with nearly equal neutral and charged impurity concentrations [6].The second is how the electrons are distributed on impurities. In the case of high temperature limit ($T = \infty$) it is a random distribution. But in the zero temperature limit the distribution is correlated, which provides the Coulomb interaction energy of system of charged acceptors, donors and electrons to be minimized. In the random electron distribution case the $1s \rightarrow 2p_{+1}$ transition line width depends on charged impurity concentration N_i only, independently on sample compensation $K = N_A/N_D$ [2-3]. In the correlated distribution case acceptors are charged taking electrons from nearest donor. Then with the same value of N_i the line width is smaller and

strongly depends on K.

Distribution transforms from the correlated to the random at temperatures [7] $k_B T \gg e^2/(\epsilon_0 \cdot r_m)$ ($r_m = (4\pi/3N_i)^{1/3}$ is the mean distance between charged impurities, ϵ_0- static dielectric constant, k_B - the Boltzman constant). In the case of strong inhomogeneous impurity system they are collected into the clusters, which have higher ionized impurity concentration (because of pure regions are between them) than that of mean value for all sample, determined from Hall measurements. Note that only these clusters are optically active for impurity absorption of radiation. So, strong inhomogeneous in the impurity distribution must cause an additional broadening mechanism for impurity absorption lines.

Note that the distribution can be changed from correlated to random not with heating only , but under any external perturbation increasing the energy, for example, an electric field.

This work devoted to experimental investigations of the SIPS line broadening caused by SI inhomogeneous distribution in n-GaAs epitaxial layers obtained by liquid and gas phase epitaxy.

2   EXPERIMENT

We investigate the $1s \to 2p_{+1}$ transition line shape of residual donors in $n - GaAs$ using the laser magnetic photoelectric spectroscopy method at moderate magnetic fields up to 6.5 T. Photoconductivity spectra (PS) of samples were registered at fixed far infrared H_2O and D_2O -lasers radiation at wavelengths $\sim$ 119 and $\sim 84 mcm$ as a function of magnetic field in the intervals $(3.5 \div 3.7)T$ and $(6.0 \div 6.2)T$ correspondingly. PS were measured at different electric fields- from linear region of samples CVC up to SI break down electric field values. At electric fields smaller than the break down one the constant voltage regime ($R_{load} \ll R_{sample}$) and at the break down the constant current regime ($R_{sample} \ll R_{load}$) was used. In order the true line shape to be registered the precaution was taken the PC, which is proportional to the change of sample conductivity $\triangle\sigma$, to be linear to radiation intensity in both regimes. Parameters of samples and growth technology are given in table1.Samples of $n - GaAs$ obtained by liquid phase (LP) and gas phase (GP) growth technology were used. The PC measurements were carried out by cross-modulation method with modulation frequency of radiation intensity

750 Hz.

For samples investigated the random distribution of electrons takes place at temperatures $T \gg 20K$. So we suppose that at measurements temperature $T = 4.2K$ in the linear region of CVC the distribution is nearly correlated.

3   RESULTS AND DISCUSSIONS

The results of $1s \rightarrow 2p_{+1}$ line shape investigations for different n-GaAs samples are given in table. The width $\triangle E$ was measured at the half height of the line in magnetic unites $\triangle H$ and then it was transformed into energetic unites $\triangle E = (\partial E_{1s \rightarrow 2p_{+1}}/\partial H)\triangle H$. The rapidity of $1s \rightarrow 2p_{+1}$ transition energy increase in magnetic field $\partial E_{1s \rightarrow 2p_{+1}}/\partial H \approx 0.18 \ meV/kOe$ was determined from the two magnetic field positions (as indicated in fig 1) of this line at different laser quantum energy $\epsilon_{119} = 10.45meV$ and $\epsilon_{84} = 14.71meV$.

First we will analyze the $1s \rightarrow 2p_{+1}$ line shape at small electric fields far from the break down one.The main results are given below.

As seen from table it is hard (except the purest sample7) to find any correlation between the line width and SI concentration, on the one hand, and degree of compensation on the other hand, in the intervals $N_D \sim 10^{14} - 10^{15}cm^{-3}$, $K \sim 0.2 - 0.9$. As a rule samples obtained by LP technology have relatively broader SI $1s \rightarrow 2p_{+1}$ photoexcitation lines than those obtained by GP technology. For example in spite of higher charged impurity concentration and compensation degree in sample1, sample5 has almost twice broader $1s \rightarrow 2p_{+1}$ donors lines in the linear CVC region. This fact can be explained only by more inhomogeneous distribution of SI in LP samples. The quantities N_D and K, usually determined from Hall measurements temperature dependency,are mean values for all sample volume. When impurities are distributed homogeneously then N_D and K values in any part of sample equal to the mean values obtained from Hall measurements given in table1.In the strong inhomogeneouse distribution case in the optically active parts of sample, where absorption of radiation takes place, the impurities form clusters with higher concentration than its mean value. It is obvious that this will cause to broaden the lines.

Except the purest, all samples have symmetric line shape as it is shown in figure1 for two of them. Only very high purity sample's line shape is

asymmetric (figure2) , having nearly all width at lower energy (or higher magnetic field) side, as it must be for quadratic Stark effect broadening mechanism.

It is also notable that the line width of all samples (except the purest) with $N_D \geq 10^{14} cm^{-3}$ are not depend on magnetic field value as it can be seen from the comparison of PS at different magnetic fields for two samples shown in figure 1.But for both knowing inhomogeneouse (quadratic Stark and quadrupole-gradient) broadening mechanisms in the indicated regions of magnetic fields the $1s \rightarrow 2p_{+1}$ line width must decrease with increasing of magnetic field. Narrowing of $1s \rightarrow 2p_{+1}$ donor's lines with magnetic field increasing was observed in very pure n-GaAs samples[8].

All above given experimental results witnesses that we deal with an additional inhomogeneouse SI line broadening mechanism connected with inhomogeneouse distribution of impurities. The energy of fluctuations increases with increasing of impurity concentration and compensation degree as $E_0 \sim 0.3 e^2 N_D^{1/3} K^{1/2} \epsilon_0$ [7] and in n- GaAs at concentrations $N_D > 10^{14} cm^{-3}$ it becomes SIPS lines dominant broadening mechanism. Note that for samples used in table1 the value of $E_0 \sim 0.1 - 0.2$ meV is about experimental line width. Because of this potential depends not only on impurity concentration, but on distribution character of SI also, this broadening mechanism can be used in quality control of samples with nearly N_D and K.

This conclusion is in accordance with the results of our investigations of line width dependence on electric field. It was found that at electric fields smaller than break down the dependence of $1s \rightarrow 2p_{+1}$ SIPS line width on electric field is different for different samples.In figure 3 this dependence is shown for two samples with inhomogeneouse and homogeneous SI distribution. With increasing of applied electric field smaller than break down, we observed both- increasing as well as decreasing line width (curves 1 and 2 in fig3). At "candle"like break down region of CVC for all samples drastic narrowing of $1s \rightarrow 2p_{+1}$ SIPS lines takes place [9]. The narrowing at break down is the result of screening of charged impurity Coulomb potential by free electrons arising in result of theirs avalanche throwing from the part neutral donors into the conduction band.

If consider electric fields smaller than break down, the experiments show that only in inhomogeneous samples we have a gradual narrowing of $1s \rightarrow 2p_{+1}$ SIPS lines with increasing of electric field, as it indicated in fig.3 (curve 1).This can be explained in the following way. Far wings of line in PS corre-

spond to those neutral donors which are placed at high potential fluctuations and as a consequence around them the charged impurity concentration is higher than the mean value for sample. External voltage applied on inhomogeneous sample will distributed inhomogeneously creating more electric field values in parts of sample with higher charged impurity concentration. On the other hand in clusters with high impurity concentration the potential of ionization must be lowered (for example in Mott transition case, when $N_D \cdot a_B^* \geq 0.25$, for n-GaAs taking place at $N_D > 2 \cdot 10^{16} cm^{-3}$ the SI break down potential is zero because all donor electrons already are free). For this reason with increasing of electric field the neutral donors in clusters with high impurity concentration (which cause the PC signal far from the line center) must to be ionized the first. In turn this would cause narrowing of $1s \rightarrow 2p_{+1}$ line.

For samples with homogeneous SI distribution at fields $E < E_{bd}$ the $1s \rightarrow 2p_{+1}$ line width increase with electric field. The typical $1s \rightarrow 2p_{+1}$ line width dependence on applied voltage for GP samples is shown in fig.3 (curve1). Our comparison of theories for uncorrelated [3] ($T = \infty$) and correlated [4] ($T = 0$) electron distributions the quadratic Stark broadening calculations for GaAs sample with $N_D = 4 \cdot 10^{14} cm^{-3}$ and $K = 0.5$ shows that in the first case the charged impurities electric field distribution function $P(E^2)$ gives the $1s \rightarrow 2p_{+1}$ line an order of magnitude (20 times) broader. In the first case we take $P(E^2) = \frac{2}{\pi} E^2 \int\limits_0^\infty dx \cdot x \cdot \exp(-\beta x^{\frac{3}{2}}) \cdot \sin(E^2 x)$ after the analogy of Holtzmark distribution, where E- electric field in units of $eN_i^{2/3}/\epsilon_0$, and $\beta = \frac{14}{15}(2\pi)^{3/2}$. So, we believe that at $T = 4.2K$ an external electric field changes the electron distribution towards to uncorrelated, so that to explain the 1.5 times broadening of the $1s \rightarrow 2p_{+1}$ line, as it was observed for GP sample1. Note that as it is seen from curve 1 of fig. 3 strong increase of line width takes place near the break down field. Note that near the break down field electron distribution changes must be strong.

Another experiment directly shows that the external electric field smaller than E_{bd} considerably changes the distribution of electrons on donors. If, there are different kinds of SI in semiconductor with comparable concentrations, as it is shown in PS of samples1, 6 and 7, the real ground state would be the $1s$ state of donor having maximal chemical shift value (the first line of PS in magnetic field). As a result of this, at low temperature, when electron distribution is correlated, the acceptors must, basically, to be charged on ac-

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count of donors having minimum central cell correction (chemical shift) value (the last line of PS in magnetic field). In fig.4 the dependence on electric field is shown for the relation of intensities of these lines (S_1/S_2) indicated as 1 and 2 in PS shown in sketch. The difference in ground state energy for these donors obtained from magnetic field positions of corresponding lines ($\Delta H \sim 0.6\ kOe$) is about 0.1 meV. As seen from fig.4 the relative population of donors 1 by electrons- (S_1/S_2) increases with increasing of electric field about 10%.

The growth technology for LP $n - GaAs$ films on $p - GaAs$ bulk samples requires substantially higher temperature than for the GP samples. This is the reason why LP samples in comparison with the GP ones have more inhomogeneous SI distribution.

4   CONCLUSION

The new broadening mechanism of $1s \rightarrow 2p_{+1}$ SIPS lines were established which takes place in n-GaAs samples with $N_D > 10^{14}cm^{-3}$ and connected with fluctuations of potential arising as a result of SI inhomogeneous distribution in samples. At $E < E_{bd}$ homogeneous and inhomogeneous SI distribution in samples causes the different dependence on external electric field for line width. Results obtained extends the opportunity of n-GaAs samples quality control by SIPS method. In particular, they allows to check more homogeneous sample among having nearly equal N_D and K.

5   ACKNOWLEDGMENTS

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Samples	$N_D \cdot 10^{-14}$ cm^{-3}	$k = N_A/N_D$	$N_i \cdot 10^{-14}$ cm^{-3}	$\mu_{77} \cdot 10^{-4}$ $cm^2/V \cdot s$	$\Delta_{\frac{1}{2}}$ (μeV) $H \approx 36kOe$	$\Delta_{\frac{1}{2}}$ (μeV) $H \approx 61kOe$
1GP	4.3	0.52	4.5	10	64	70
2CP	7.3	0.65	9.6	7.3	70	80
3LP	8.7	0.53	9.0	7.3	150	160
4GP	15.0	0.38	11.0	5.7	85	90
5LP	4.22	0.36	3.0	8.6	136	140
6GP	4.3	0.52	4.5	10	62	65
7GP	high purity	-	-	-	12	8

Table 1: Parameters and widths of $n - GaAs$ $1s \rightarrow 2p_{+1}$ donors lines at linear region of CVC

CAPTIONS

Fig.1: (fig1.gif)

PC as a function of magnetic field for sample1 (lower PS) and sample3 (upper PS) at $\lambda \approx 119\mu$ (left) and $\lambda \approx 84\mu$ (right) wavelengths radiation. Applied voltage is about $1V$.

Fig.2: (fig2.gif)

PS of different donors of high quality sample7 ($\lambda \approx 119\mu$). The line width is not depends on applied voltage, as in the case of [8].

Fig.3: (fig3.gif)

Electric field dependence of $1s \rightarrow 2p_{+1}$ line width of two samples ($\lambda \approx 119\mu$): 1 - sample1; 2 - sample5; 3 - CVC of sample1 at $E \perp H$ and $H = 36.5$ kOe. Sample 5 has nearly the same CVC. Distance between contacts is about $3\ mm$.

Fig 4: (fig4.gif)

The electric field dependence of two shallow donors $1s \rightarrow 2p_{+1}$ lines intensity relation S_1/S_2,which ground state energy difference is ~ 0.1 meV .The PS is shown in sketch (sample ,6).

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